Journal of Magnetism and Magnetic Materials 322 (2010) L19–L24

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Letter to the Editor

Ferromagnetism and spin reorientation in $Sm_{12}Fe_{14}Al_5$

S. Mizusaki [a,*], N. Kawamura [a], T. Taniguchi [a], Y. Nagata [a], T.C. Ozawa [b], A. Sato [c], Y. Noro [d], H. Samata [e]

[a] College of Science and Engineering, Aoyama Gakuin University Fuchinobe, Sagamihara, Kanagawa 229-8558, Japan
[b] Nanoscale Materials Center, National Institute for Materials Science Namiki, Tsukuba, Ibaraki 305-0044, Japan
[c] Materials Analysis Station, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[d] Kawazoe Frontier Technologies, Co. Ltd., Kuden, Sakae, Yokohama, Kanagawa 931-113, Japan
[e] Faculty of Maritime Sciences, Kobe University Fukaeminami, Higashinada, Kobe, Hyogo 658-0022, Japan

ARTICLE INFO

Article history:
Received 5 November 2008
Received in revised form
5 December 2009
Available online 22 December 2009

Keywords:
Rare earth intermetallic
Magnetic anisotropy
Spin reorientation
Flux method
Single crystal

ABSTRACT

The single crystal of the new ternary compound $Sm_{12}Fe_{14}Al_5$ was grown and its crystallographic and magnetic properties were investigated. $Sm_{12}Fe_{14}Al_5$ has a hexagonal structure of the space group *p-3m1* and shows ferromagnetism with a Curie temperature of 245 K. The easy direction of magnetization is parallel to the *c*-axis at temperatures between 245 and 85 K; however, it changes to the *c*-plane below 85 K through a first-order-like phase transition. No saturation is observed in the magnetization curve even under the applied field of 55 kOe at 5 K. $Sm_{12}Fe_{14}Al_5$ seems to have a large coercive field at very low temperatures. The anisotropy field was estimated at 5 and 120 K and the saturation magnetization of low temperature phase is explained assuming a ferromagnetic coupling between Fe and Sm sublattices.

1. Introduction

There are many interesting magnetic intermetallic compounds in the systems composed of rare-earth and transition metal elements. Among these compounds, the Sm–Fe system has attracted attention because high-performance hard-magnetic properties were found in the $Sm_2Fe_{17}N_3$ system [1]. Furthermore, in recent years, many interesting phenomena, such as large magnetoresistance, anomalous electron-scattering effects, and a magnetocaloric effect have been found in a ternary system containing rare-earth elements [2–6]. Thus, from fundamental and practical viewpoints, it seems very important to search for new functional compound in a ternary system containing rare-earth metals. Among ternary systems, the R–T–M (R=rare-earth metal, T=transition metal, M=Al or Ga) system is interesting because a large magnetocaloric effect and magnetoresistance have been observed in the Pr_2Ni_2Al-type orthorhombic compounds of Gd_2Co_2Al and Gd_2Co_2Ga near the ferromagnetic ordering temperature of 77 K [7]. Therefore, there is a quite possibility to discover new interesting materials in the Sm–Fe–Al system. However, although study on the Sm–Fe–Al system has been performed for $Sm_2Fe_{17-x}Al_x$ system to improve hard magnetic properties of Sm_2Fe_{17}[8–12], study on the Sm–Fe–Al system is still lacking. There is much left to study on this system from physical and practical standpoints.

This study was conducted to synthesize the crystal of a new ternary compound in the Sm–Fe–Al system and a new interesting ferromagnetic ternary compound was discovered successfully. In this paper, the crystallographic and magnetic properties of the compound are reported.

2. Experiment

Single crystals were grown with a modified flux method using samarium as a flux [13]. After arc-melting an appropriate amount of high-purity (99.9%) samarium, iron, and aluminum the mixture (~30 g) was placed in a BN-coated alumina crucible with a very small amount of iron powder and samarium. The crucible was further sealed in a quartz ampoule after evacuating to 1.5×10^{-4} Torr. The mixture was heated to 1075 °C in 10 h. After being held at that temperature for 2 h, it was cooled to 920 °C at a rate of 40 °C/h and subsequently cooled to 820 °C at a rate of 0.7 °C/h. The mixture was removed from the furnace and cooled to room temperature.

The chemical composition of the crystals was estimated by electron-probe microanalysis using wavelength dispersive spectrometers. The crystal structure was characterized by using single-crystal X-ray diffraction. X-ray diffraction data were acquired on a Bruker SMART APEX S diffractometer equipped with a graphite monochrometer at room temperature. A crystal (0.34 mm × 0.28 mm × 0.24 mm) was mounted on a glass fiber. X-ray was generated using a Mo target at 40 kV and 40 mA. A total of 12,785 reflections were collected for the full sphere using a 0.3° ω-scan with a 30 s exposure. The crystal structure was solved by direct methods using SHELXS-97 and refined utilizing SHELXL-97

---

[*] Corresponding author. Tel.: +81 42 759 6255; fax: +81 42 759 6523.
E-mail address: smizusaki@ee.aoyama.ac.jp (S. Mizusaki).

0304-8853/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2009.12.021

software package using 1395 unique reflections and 37 parameters [14]. The magnetization was measured by a SQUID magnetometer using as-grown crystals at temperatures between 5 and 350 K under applied magnetic fields of up to 55 kOe.

3. Results and discussion

3.1. Crystallographic properties

Single crystals were grown on a surface of cavities generated in the cooling process. The crystals could be removed without applying any excessive stress since they were standing on the surface of the cavity. Fig. 1 shows (a) a photograph of an as-grown crystal and (b) a photograph of an X-ray Laue back-reflection taken in a geometry in which the incident X-ray beam is perpendicular to the hexagonal plane. The as-grown crystal has a shape of hexagonal prism and the Laue pattern has clear three folds symmetry. The composition ratio Sm:Fe:Al of the crystal was estimated to be 2:2:1 by electron-probe microanalysis (EPMA). The results of the single-crystal X-ray diffraction study for the as-grown crystal showed that the crystal has a hexagonal structure of space group *p-3m1*. The refined crystal structure parameters obtained by the X-ray diffraction study are listed in Table 1, and a possible crystal structure drawn using the parameters is shown in Fig.2. It is seen that the crystal has unique crystal structure in which $AlSm_6$ octahedrons order along the a- and b-axes with Sm in common, and Fe-icosahedrons with center Fe atom order in the *c*-axis. The refined composition of the crystal was $Sm_{12}Fe_{14}Al_5$. Although this composition differs slightly from that estimated by EPMA, we concluded that $Sm_{12}Fe_{14}Al_5$ is the actual composition of the crystal.

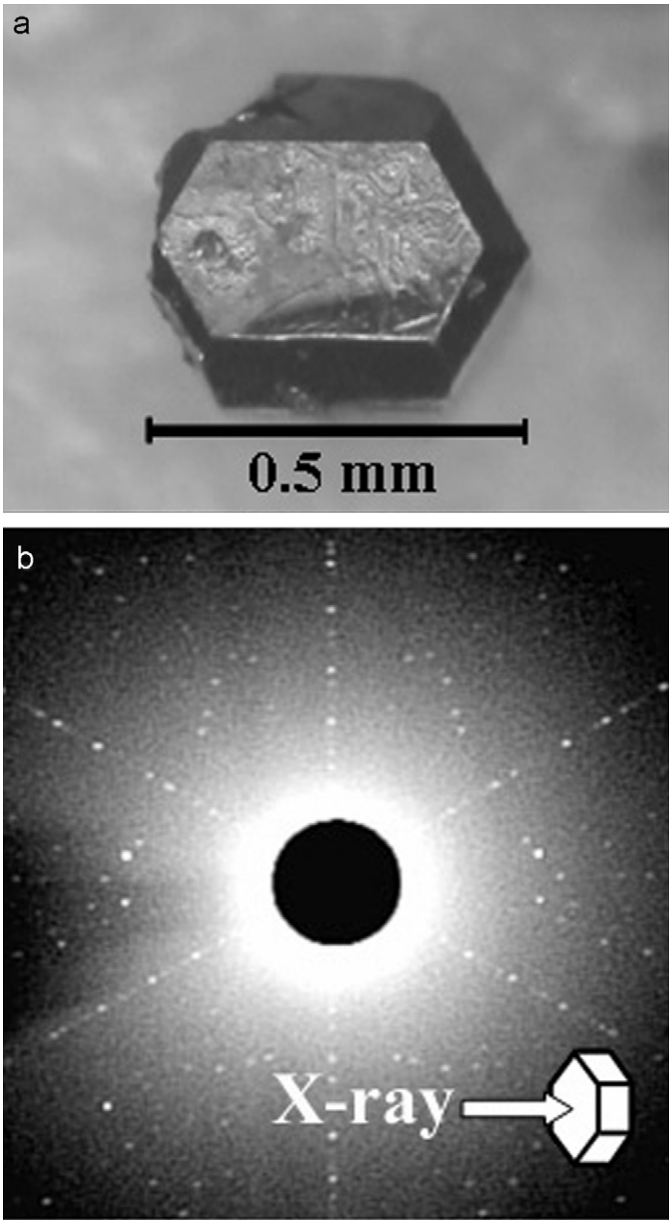

Fig. 1. (a) photograph of the as-grown crystal and (b) photograph of an X-ray Laue back-reflection taken in a geometry in which the incident X-ray beam is perpendicular to the hexagonal plane of the crystal.

3.2. Magnetic properties

Fig. 3 shows the temperature dependence of the magnetization measured for a $Sm_{12}Fe_{14}Al_5$ crystal in a field of 1 kOe applied parallel to the specific crystal directions. When the magnetic field is applied to the direction perpendicular to the *c*-axis, very small magnetization is observed at 5 K. However, the magnetization increases remarkably above 60 K and, after reaching a maximum at about 80 K, decreases and disappears at about 90 K. The thermomagnetic process observed in the *c*-plane is irreversible. In the cooling process, the magnetization increases suddenly below 90 K and is saturated almost below 80 K. On the other hand, when the field is applied parallel to the *c*-axis, almost no magnetization is observed at 5 K, as in case of the *c*-plane; however, the magnetization appears suddenly at about 80 K, and, after showing a gradual decrease, it disappears at about 250 K. This thermomagnetic process is reversible. The $M(T)$ curve between 90 and 250 K has similar characteristics to those of ferromagnets. The Curie temperature T_C was determined to be 245 K from the $dM(T)/dT$ curve. The $M(T)$ curves in both directions have almost identical characteristics above 270 K.

The transition observed at a temperature between 80 and 90 K is considered to be a spin reorientation (SR) transition. The spin reorientation temperature was determined from the $dM(T)/dT$ curve as 85 K. From the $M(T)$ curves obtained in the directions parallel and perpendicular to the *c*-axis, it is clear that the easy axis of magnetization reorients from the direction parallel to the *c*-axis to the *c*-plane. A similar spin reorientation was observed for samarium compounds of tetragonal $Y_{2-x}Sm_xFe_{14}B$, cubic $SmFe_2$, and hexagonal $SmFe_3$[15–17]. The reorientation of $Sm_{12}Fe_{14}Al_5$ occurs in a very narrow temperature range; therefore, the transition is considered to be first-order magnetic phase transition. This type of first-order phase transition was observed in rare-earth compounds, such as orthoferrite ($DyFeO_3$) [18], $Er_2Fe_{14}B$, and $Tm_2Fe_{14}B$ [19]. In particular, spin reorientation from the *c*-axis to the *c*-plane was observed for $Er_2Fe_{14}B$ and $Tm_2Fe_{14}B$. It is well accepted in theoretical studies on the tetragonal rare-earth-transition-metal compounds $R_2Fe_{14}B$ (R=rare-earth metal) [20] that the easy direction of magnetization is in the *c*-plane for R=Pr, Nd, Tb, Dy, and Ho and perpendicular to the *c*-axis for R=Sm, Er, and Tm at room temperature. The spin reorientation of $Er_2Fe_{14}B$ and $Tm_2Fe_{14}B$ has been explained to occur through the competition between the planar anisotropy of rare-earth ions and the uniaxial anisotropy of the iron sublattice.

In case of $Sm_{12}Fe_{14}Al_5$, since the Sm:Fe ratio is about 1:1 and the Fe anisotropy is about two orders of magnitude weaker than that of Sm even at high temperatures, the Fe sublattice anisotropy should be rather weak and cannot provide a large anisotropy to compete with that of Sm sublattice at a temperature that is approximately 30% of T_C. Therefore, another reason must be considered for the reorientation observed in $Sm_{12}Fe_{14}Al_5$. There